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Its primary objectives are to ensure the long-term availability of timber supplies; to optimize timber uses; and to contribute to the growth and diversification of Alberta's economy.

The Agreement comprises three programs: Reforestation; Applied research, technology transfer and opportunity identification; and Public information, evaluation and administration. These programs are managed by a joint Directorate and are implemented by the Canadian Forestry Service and the Alberta Forest Service.

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Ses objectifs principaux sont assurer la disponibilité à long terme de réserves de bois; optimiser leur utilisation; et contribuer à la croissance et la diversification de l'économie de la province.

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For more information, please call or write:

Pour de plus amples informations, veuillez vous adresser à:

Canadian Forestry Service
Northern Forestry Centre
5320 - 122 Street
Edmonton, Alberta
T6H 3S5
Telephone: (403) 435-7210
Attention: S. Price

OR/OU Alberta Department of
Forestry, Lands & Wildlife
9915 - 108 Street
Edmonton, Alberta
T5K 2C9
Telephone: (403) 427-3583
Attention: D. Fregren

BONDING WOOD COMPOSITES WITH ISOCYNATES

P.R. Steiner
Forintek Canada Corp.[1]
1986

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[1]Vancouver, B.C.

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T6H 3S5

SUMMARY

Isocyanates are highly reactive compounds which have recently gained prominence in the bonding of wood composites, especially particleboard. Both positive and negative features have been associated with the use of these adhesives.

On the positive side, isocyanates:

- are relatively rapid curing both at hot press and room temperature conditions,
- provide good strength properties,
- are tolerant to higher moisture content furnish,
- have no formaldehyde emissions.

The negative aspects are:

- high cost,
- potential health and handling hazards,
- tendency to stick to press cauls and platens.

A review of isocyanate chemistry established that the reactions most relevant to wood bonding involve isocyanate-wood hydroxyl and isocyanate-water interactions. The former leads to polyurethane products, while the latter produces polyurea linkage. Currently, polymeric methylene-diphenyl-diisocyanate (MDI), as a 100 percent non-volatile liquid or as a water-emulsion, is used almost exclusively for wood bonding. There are three suppliers of this material in North America.

Isocyanates have been used commercially in Europe since 1973 but have only been used in North America since 1979. Part of this delay was due to concern over handling and safety considerations. While most experience with isocyanates has been in the bonding of particleboards, laboratory studies have indicated that isocyanates can also be effective bonding agents for waferboard and oriented standboard. A review of available information was undertaken which revealed a number of important factors influencing isocyanate board manufacture and properties. These factors include storage and handling, application techniques, wood moisture content, resin content, cure and durability. The issue of optimal furnish moisture content is one of the most controversial factors.

Future trends in wood composite board manufacture suggest an increasing use of isocyanate binders, especially as isocyanate prices decrease. A number of options, such as steam injection pressing and catalyst incorporation, are available, which may further increase cure speed and bond performance of isocyanate panels.

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INTRODUCTION

Isocyanates are highly reactive compounds commonly used in the preparation of polyurethanes. Consequently, the chemistry and application technology of isocyanates is closely linked to that of polyurethanes or urethane polymers. While isocyanates have been available for over 30 years and used extensively in the plastics industry, their application as commercial wood adhesives is a recent occurrence. The reason for this delay relates to high chemical costs, moisture sensitivity, toxicity and special application methodology commonly associated with isocyanates. Increased emphasis on process efficiency in the wood industry, together with the reduction of isocyanate costs due to expanded production capacity, has enhanced isocyanate use in wood bonding.

Ironically, the highly reactive nature of isocyanates leads to some of the problems associated with their industrial applications. Often they are too reactive, not only bonding wood together but also adhering the wood panel to press platens. Thus, effective use of this material as a bonding agent requires an awareness of the chemistry involved in isocyanate reaction and precautions needed in handling this material, and an appreciation of present and future opportunities for bonding wood with isocyanate. This report is intended to give a perspective on isocyanates in terms of some of these issues as related to wood composites.

It should be recognized that any discussion of isocyanates is complicated by the variety of types available (Pigott, 1969). Not only can these systems be divided into inorganic and organic materials, but the latter can be further subdivided into aliphatic and aromatic types. These isocyanates can also be in the form of monomers, dimers or polymers. As polymers, the system can be characterized as one-component or as a copolymer with two-component or multi-component combinations. The isocyanate system discussed here will be restricted to the one presently used almost exclusively for wood bonding. This type is referred to specifically as methylene-diphenyl-diisocyanate, or MDI.

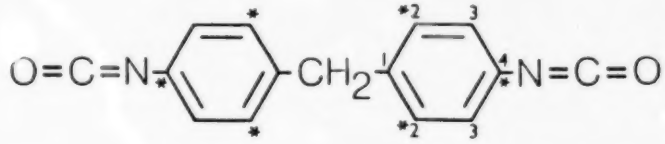
2.0 STAFF

P.R. Steiner — Research Scientist
Composites Department

3.0 CHEMISTRY OF MDI

3.1 REACTIONS (Frisch et al., 1983; Motoki et al., 1984)

As a monomer, MDI has the following general chemical structure:

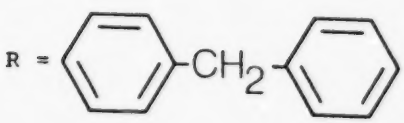


There are two isocyanate groups on the molecule (difunctional) and these can reside on the 2 or 4 positions of the aromatic ring (shown as indicated or by *). The difunctional character of the molecule provides its crosslinking capabilities. This compound has a low vapor pressure making it essentially non-volatile under most wood bonding conditions--an important consideration in plant operations. Since monomeric MDI is a semi-solid compound, practical applications dictate that it be used in its so-called polymeric MDI form, which is a liquid with a 100 percent non-volatile content. This is most often a mixture of dimers, trimers and tetramers. The variety of ways these units can be linked results in a number of different types of polymeric MDI with varying reactivities and viscosities. Low viscosity polymeric MDI's are favored for wood composite binders because of requirements for spray application.

The highly unsaturated isocyanate group (- N = C = O) is extremely reactive with a large number of materials. The reaction proceeds with almost any compound having an active hydrogen (i.e., one that can readily exchange). These include compounds with hydroxyl, amine, phenol, carboxylic acid, urea and urethane groups. From a wood bonding perspective the two most important reactions occur between isocyanate and hydroxyl groups and isocyanate and water. Hydroxyl groups are present in large quantities in cellulose, lignin or hemicellulose portions or wood. The general reaction sequence proceeds as follows:

URETHANE

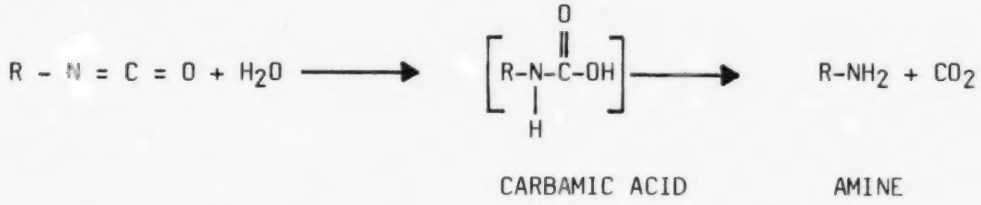
Where,



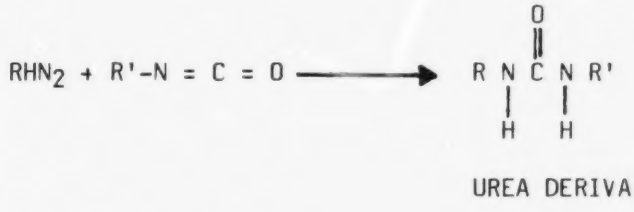
The remaining isocyanate group can further react with another wood hydroxyl unit while the hydrogen atom now attached to the nitrogen is

sufficiently active to allow additional isocyanate molecules to react at this position. In this manner, a crosslinked system can be formed. This reaction product results when little or no moisture is present.

The presence of water can alter the isocyanate reaction sequence in the following manner:



The carbamic acid intermediate is unstable and readily decomposes to an amine and carbon dioxide gas. The resulting amine product is highly reactive with other isocyanates, forming polyurea:



Active hydrogens in this urea product can, in turn, further react with other isocyanate molecules, resulting in branched and crosslinked structures. When large quantities of water are present, the dominant polymeric structure will be a polyurea rather than a polyurethane. With high moisture content (mc) wood, resulting reaction products may well depend upon relative activity of the exchangeable hydrogens, concentration of reactants and reaction temperature.

Primary hydroxyls will be more reactive than secondary ones, which in turn will be more reactive than a tertiary hydroxyl. The relative reaction rate of water with isocyanate is similar to that of a secondary hydroxyl. Compounds containing amine groups are one of the fastest reaching molecular species with isocyanates. Consequently, wood mc plays an important role in isocyanate-bonded composites since, as shown above, highly reactive amines can be produced which can help accelerate polymerization in the system. While this may appear advantageous, it should be recognized that too much water can convert substantial quantities of isocyanate to polyureas and leave few terminal isocyanate groups available to produce bonding urethane linkages between adhesive and wood. This condition could have a severe impact on the overall bond quality and durability of the wood composite.

3.2 CATALYSTS (ACCELERATORS)

While isocyanates react much faster than phenol formaldehyde (PF) adhesives under normal board pressing conditions, their cure speed may be too slow when pressing temperatures are decreased to accomodate higher mat mc or when cold pressing is utilized. Catalysts can be employed to achieve faster cure under these conditions. Alternatively, by proper choice of catalysts the relative proportion of polyurethane bonds (from wood hydroxyl-isocyanate reactions) to that of polyurea bonds (from water-isocyanate reactions) can be adjusted during cure (Pigott, 1969). Catalysts can also be used to enhance the degree of crosslinking, thus providing improved bond strength and durability properties.

While present cost and application difficulties have discouraged catalyst use in isocyanate bonded wood composites, many catalyst systems have been utilized in the production of polyurethane plastics. Tertiary amines and organometallic compounds, especially of the tin type, are the most commonly employed catalysts. The mechanism by which these catalysts activate the isocyanate is complex and will not be discussed here (Frisch et al., 1983). Generally, catalytic activity increases as the basicity of the catalyst increases. Some catalysts used to increase the isocyanate-hydroxyl reaction rate are listed in Table 1.

3.3 COMMERCIAL SUPPLIERS

The number of chemical companies capable of supplying large quantities of polymeric MDI in North America is limited to three; Mobay, Rubicon, and Dow Chemicals. Mobay is a subsidiary of Bayer A.G. of West Germany. Rubicon is a subsidiary of the United Kingdom firm ICI. Dow Chemicals has recently become a polymeric MDI supplier through its acquisition of UPJOHN Co. chemical division. The tradenames for polymeric MDI products recommended for wood bonding by each of these companies are listed in Table 2. Another West German company, BASF, is also a major supplier of polymeric MDI in Europe.

3.4. HANDLING AND SAFETY ASPECTS

Isocyanates are potentially hazardous materials and care must be taken in their handling. Isocyanate vapors can be a principle problem because they can severely irritate eye, nose, throat and lung membrane. The extent of hazard from vapor depends on the vapor pressure of the particular isocyanate. Polymeric MDI has a relatively low vapor pressure at normal temperatures so that it is difficult for vapor concentration to reach the maximum threshold limit value (TLV) allowed in the workplace. This value is currently set at 0.02 ppm by the International Isocyanate particleboards were being produced showed no values exceeding this prescribed limited when adequate ventilation was present in the plant (Ellingson, 1985; Frink and Layton, 1985).

The most hazardous area for polymeric MDI exposure in a waferboard/oriented strandboard (OSB) plant occurs during spray blending operations where airborne droplets are present. Containment of the adhensive aersol in a sealed blender and effective ventilation around this

Table 1

Some Isocyanate Catalysts

Tetramethylbutane diamine (TMBDA)	
Triethylamine	
Dibutyl tin dilaurate	increasing hydroxyl-isocyanate reactivity
Dimethyl tin acetate	
Stannous octaacetate	
Stannous octaacetate + TMBDA	

Table 2

Polymeric MDI Products for Wood Bonding

Company	Tradename
MOBAY	Mondur MR Mondur E-463 (emulsion) Mondur E-441 Desmodur PU 1520
RUBICON	Rubinate MF 178 (emulsion) XI-197 (self-releasing)
DOW (UPJOHN)	ISOBIND 100

area is essential. Another hazard is dust particles to which adhesive droplets can be attracted and thus possibly inhaled by workers.

While many concerns exist about isocyanate exposure it should be recognized that these materials are widely used in a variety of industries and that a number of well-defined procedures have been developed for their handling. These procedures involve: good ventilation, containment of airborne droplets, use of protective clothing and installation of chemical monitoring devices. Workers involved with adhesive handling and blending should wear protective overalls, rubber gloves and goggles or face shields.

Handling for MDI chemicals should only be undertaken by people who are familiar with the potential hazards and who understand how to clean and decontaminate spills. Some of the properties of polymeric MDI are listed in Table 3 and a typical product data sheet is presented in Appendix I.

The major concern during storage of polymeric MDI is to prevent entry of water (either in liquid or vapor form). Water floats on the surface of polymeric MDI and reacts slowly with it at temperatures below 40°C. This reaction becomes more vigorous at higher temperatures, generating additional heat and releasing carbon dioxide vapor, which can lead to a build-up of pressure within a closed container.

A standard solution useful for deactivating isocyanates by converting them to relatively harmless polyureas involves a mixture of 90 percent water, eight percent concentrated ammonia and two percent liquid detergent by weight.

3.5 BONDING OF WOOD

3.5.1 Historical Developments

The first commercial use of polymeric MDI to bond wood was in the production of a German particleboard in 1973 (Deppe, 1977). Prior to this, extensive laboratory testing established isocyanates as satisfying the V-100 requirement of the German DIN particleboard standard (Schriever, 1982). Initial goals were to produce composites with properties equal to phenolic boards. Experience soon demonstrated that this could be achieved with added benefits of faster cure times, greater tolerance to wood mc and better dimensional stability (Adams, 1981; Ernst, 1985). It was also recognized that releasing agents, or a three-layer board having surface layers bonded with conventional urea formaldehyde (UF), phenol formaldehyde (PF) or melamine urea formaldehyde (MUF) adhesives were required to prevent the mat from bonding to the metal cauls or platens (Cohen and Galbraith, 1983).

Due to high chemical costs, European applications of isocyanates for bonding wood continued at a slow pace during the period of 1973 to 1978. During 1979, the first North American commercial plant using isocyanates in a particleboard composite was constructed by Ellingson Lumber Co. in Oregon (Ellingson, 1985). This plant used planar shavings as furnish and

Table 3

Polymeric MDI Properties

Physical State at 25°C	Oily liquid
Viscosity (m Pas)	200 - 300
Color	dark brown
Specific Gravity	1.23
Boiling Point (°C)	Polymerizes above 260 with carbon dioxide release
Flash Point (°C)	above 200
Freezing Point (°C)	below 10
Vapor Pressure (mbar at 25°C)	below 10^{-4}

produced a board called "Elcoboard" that had a veneer surface layer that protected the panel from sticking to the press. More recently, this company has been producing an all particleboard panel (Isobind trademark) and using releasing agents to overcome sticking problems (Ellingson, 1985).

During the early part of the present decade, isocyanate usage as wood binders increased dramatically in Europe, due in most part to the more stringent restrictions on formaldehyde emissions in composite boards (Ernst, 1985). Isocyanates were now being used to replace UF adhesives in particleboard. To control blinder costs, isocyanates were often applied as co-binders with PF or UF, being sprayed separately or mixed and sprayed together on furnish. Although currently used in about a dozen particleboard plants in several European countries, the commercial use of isocyanates for wood composites should be considered in its infancy.

North American experience with isocyanates is limited and primarily directed towards waferboard and OSB applications (Adams, 1981; Frink and Layton, 1985). Several mill trials have been continued at Canadian waferboard plants (i.e., Waferboard Corp., Timmins and Grand Waferboard, Englehart). The impetus to use isocyanates for waferboard has been to provide more flexibility in flake mc, improve bonding of higher density hardwoods, improve press times (especially with thicker boards) and to produce a lighter-colored board. This author is not aware of any plant manufacturing a completely isocyanate-bonded waferboard panel at this time. Limited production has taken place using isocyanates in the panel core.

A continuing concern with isocyanate for waferboard is to efficiently apply the binder onto flakes. For cost reasons resin contents below 1.5 percent are needed but suitable spray equipment to achieve adequate resin coverage at these levels for waferboard is presently not available. The question of improved resin coverage at low board binder contents has led to the development and use of emulsified polymeric MDI solutions (often referred to as EMDI). Here, polymeric MDI and water are mixed in a high speed stirrer at a 1:1 or 1:2 ratio together with an emulsifying agent which acts as a stabilizer (Adams, 1980; Ernst, 1985). These emulsions are stable for one to two hours and allow more effective binder coverage of wood. Emulsions have the further advantages of low viscosity and not requiring anhydrous conditions during handling.

3.4.2 Important Factors Influencing Board Manufacture and Properties

Both laboratory and industrial experience with polymeric MDI as a wood bonding agent have established a number of prominent factors governing the resin application and board properties of isocyanate-wood composites. In some cases there is only a limited understanding of some of these factors, but it can be anticipated that knowledge in these areas will expand as usage of isocyanates for wood increases. Based on present information the important factors to consider are summarized as follows:

Storage and Handling of Isocyanates. As can be appreciated from discussions in Section 3.4, this issue will require continual attention. Both federal and provincial government and Workers' Compensation Board

rules on use of isocyanates will need to be satisfied. Storage containers and transfer lines will need to be kept sealed from moisture. Good ventilation and dust control is essential especially around the blender and press areas. Atmospheric monitoring devices should be present in the plant. Staff using isocyanates will require special training.

In the laboratory, resin blending operations should be carried out in a separate room with respirators worn during spraying operations. Resin-coated flakes should be handled mechanically or with rubber gloves. Good ventilation should exist around the press.

Adhesive Costs. Isocyanate production is affected by petroleum costs. Current polymeric MDI costs in carload quantities are about 91 ¢/lb US ($1.26 CAN). Thus, isocyanate costs are about 2.5 times that of phenolic resin. This relative cost ratio has decreased over the last five years as production volume of polymeric MDI increased. The relative current cost of isocyanate to other wood adhesives are given in Table 4 in US dollars.

Cost savings are possible by employing copolymers of isocyanate with conventional PR, UF or MUF adhesives or combining isocyanates with polyol compounds or lignin. These combined systems, however, tend to be more limited in their application and bonding conditions.

Application Technology. While liquid systems can be easily sprayed onto particleboard furnish, uniform resin coverage in waferboard is difficult. Spinning disc applicators have so far provided the best resin coverage. Two types of polymeric MDI have been used; regular and emulsified. The former contains 100 percent non-volatiles while the latter is mixed with at lease an equal weight of water.

Formation of EMDI greatly reduces resin viscosity, thus enhancing sprayability which in turn results in improved bonding performance (Ball, 1981; Cohen and Galbraith, 1983). Many commercial board producers are tending to favor EMDI over standard MDI types. Since water reacts slowly with MDI at room temperatures, formation of the emulsion is usually accomplished using automatic mixing equipment just prior to resin application (Ernst, 1985).

As a consequence of isocyanate reactivity at moderate temperatures, greater care must be taken in controlling the processing time and temperature of flakes during blending, layup and pressing. Table 5 indicates the extent to which internal bond (IB) properties can change with storage time and temperature of resin-coated particles (Ernst, 1985). Flake mc will also influence storage life.

Isocyanates are also noted for having poor tack properties. The present use of wax and mat transfer techniques used for waferboard appear to make this a problem which can be readily overcome.

Sticking Problems. Concern over the tendency of isocyanates to react with metals has led to a number of development to prevent panels from sticking to press platens. One technique uses a three-layer board having isocyanate in the core layer and PF resin bonding the face layers (Udvardy, 1979). This has the advantage that the PF layer will not stick

Table 4

Average Current Price (1986) of Wood Adhesives

Adhesive	US price ($/lb)
PF (100% liquid)	0.36
PF (powder)	0.48
Polymeric MDI	0.91
UF (100% liquid)	0.15

Source: Chemical Marketing Reporter. Schnell Publishing co., N.Y. June, 1986.

Table 5

IB Dependence on Furnish Storage Time and Temperature after Resin Application

Storage Conditions		IB (M Pa)	
Time (hrs)	Temp. (°C)	Dry	After Boiling
0	20	0.75	0.21
1	"	0.74	0.21
5	"	0.71	0.20
10	"	0.68	0.19
0	50	0.75	0.21
1	"	0.72	0.18
5	"	0.55	0.10
10	"	0.37	0

to the platen but will still cure rapidly because of its proximity to the hot press platen. Alternatively, the board's outer layer can be a wood veneer or other overlay which prevents isocyanate adhesive from migrating to the panel surface (Ellingson, 1985).

Initially, chemical techniques to prevent sticking involved coating cauls and/or board faces with a releasing agent, usually composed of Teflon derivatives or stearic acid salts. More recently, release agents are being incorporated directly into the isocyanate resin (Cohen and Galbraith, 1983).

Co-polymers and Additives. Co-polymers of isocyanate with UF, MUF and PF adhesives have been utilized to either reduce binder costs or control formaldehyde emissions (Ernst, 1985; Schriever, 1982). This is often accomplished by spraying each resin component separately onto wood particles in a blender. Developments in EMDI technology should now make it possible to premix these co-polymers prior to spraying. Separate co-application of PF and isocyanate resins have also been tried in waferboard, with significant benefits reported in improving cure and bond strength (Hse, 1978).

Addition of wax to waferboard is a common procedure used to enhance water resistance in a board. The type of wax employed can influence the bonding properties of the isocyanate (Deppe, 1977). With wax emulsions, consideration must be given to the amount of extra water added to the wafers by this mixture, since this water can interact with isocyanate. Regular hot wax should be neutral or acid stabilized to be compatible with isocyanates. Alkaline waxes can greatly accelerate the isocyanate-water reaction.

Wood Moisture Content. The fact that some moisture is present in all wood and that isocyanates react with water is the most important factor governing the bonding of wood composites with isocyanates. This issue is complicated further by moisture content variations commonly found in sections of wood and the possibly that water may exist in either bound or free forms.

A number of studies have reported that the primary advantage of using isocyanate binders is their greater tolerance to higher mc furnish (Ball, 1981; Deppe, 1977; Ernst, 1985; Johns and Wilson, 1980; McLaughlin, 1980). In fact isocyanates seem to bond most effectively with wood at 8 to 12 percent mc. A point of controversy, however, is the maximum mc which can be accommodated (Deppe, 1977), while others suggest that bond quality deteriorates above a 10 to 12 percent mc level (Johns, 1982). From minimum mc consideration, the general concensus is that mc below five percent is detrimental to developing good isocyanate bond quality. Rationalizing these seemingly conflicting statements about mc effects in the published literature can present a formidable task. Consideration of basic chemical reactions if isocyanates does provide some insight into the situation.

As discussed before, isocyanates react with any compound containing active hydrogens, including water. While the water-isocyanate reaction is slow at room temperature it is accelerated above 50°C and by the presence

of catalytic materials such as acids, bases and metal ions which may be available in small quantities in wood. Since composites, like waferboard and OSB, are manufactured at high pressing temperatures, a greater probability exists for this water reaction to occur with subsequent polyurea formation. If the water-isocyanate reaction dominates, the potential exists to convert most of the isocyanate to polyurea and carbon dioxide. In practise this is unlikely, since the isocyanate-wood hydroxyl reaction is also fast at elevated temperatures, leading to the formation of polyurethane bonds. Some quantitative information on the relative proportion of polyurea to polyurethane bonds formed during particleboard pressing has been determined from carbon dioxide gas release measurements and is presented in Table 6 (Wittmann, 197f).

Assuming this data can be extrapolated to waferboard conditions of 12 percent mc and a range of 1.5 to 2.0 percent resin content, then approximately 50 percent of the isocyanate could be converted to polyureas during bond formation. While initial reports suggested that 25 percent mc conditions could be used without influencing particleboard bond quality more recent experience indicates that an mc range of 6 to 15 percent may be more appropriate for waferboard or OSB (Johns, 1982). Consequently, a limited amount of polyurea formation may be desirable to strengthen bonds between polyisocyanate compounds, but too much polyurea formation will inherently weaken the board (especially IB) because of reduced polyurethane-wood bond formation.

The mc issue is further complicated by the realization that amines are produced by the initial reaction of water with isocyanate and that these amines can accelerate the speed of the isocyanate wood reaction (Pigott, 1969). This is an added benefit of having some moisture present. A further question still unresolved concerns the relative activity of water in its free or bound state. Expectations are that free water would be more available for reaction than bound water. Thus, wood flakes with idential mc adjusted either by water spray or by slowly equilibrating the furnish in a humidity chamber may react with isocyanate in a different manner.

Resin Content. With good spray coverage isocyanates can be used at lower resin contents than PF resins to achieve similar bond properties. Resin quantities required depend upon furnish flake or particle size. In particleboard, where PF levels of eight to nine percent are needed to satisfy requirements of the German V-100 DIN standard, polymeric MDI levels of five to seven percent are sufficient (Deppe, 1977; Ernst, 1985).

For waferboard, panels with isocyanate resin levels ranging from 1.5 to 3.0 percent have been manufactured and tested (Adams, 1981; Frink and Layton, 1985; McLaughlin, 1980). Results suggest that resin levels below 1.8 percent are unsatisfactory, especially in terms of meeting IB requirements (Adams, 1981). It should be remembered that one of the difficulties in conducting these tests is associated with attaining uniform flake coverage at lower resin levels. Tests with OSB panels have involved resin contents of 2.0 to 4.4 percent, with about a 2.8 percent level being the minimum required for suitable board properties (Adams, 1981). Overall trials have confirmed that resin levels can be reduced by

Table 6

Reaction of Isocyanate with Water, in Particleboard Pressed at 165°C, as Determined by Carbon Dioxide Gas Release
(Wittmann, 1976)

Wood mc (%)	Resin Content (%)	NCO Consumed by Water (%)	Projected Ratio Polyurethane/Polyurea
15	3	33	2.0
3	4	18	4.5
6	"	23	3.0
12	"	28	2.6
15	"	30	2.3
3	6	14	6.1
6	"	20	4.0
12	"	25	3.0
15	"	27	2.7

about 20 percent in isocyanate compared to PF boards using present application equipment (Frink and Layton, 1985; Udvardy, 1979).

Cure. The ability to cure isocyanates at conditions ranging from room temperature (i.e., 25°C) to hot press temperatures (i.e., 200°C) makes this an extremely flexible system for board manufacture. In terms of relative cure speed, isocyanates are somewhat comparable to PRF adhesives but with the added benefit of being a one-component system, light in color and less sensitive to moisture during cure.

As previously mentioned, water will influence the type of reaction taking place and this affects cure speed. Under certain temperatures (i.e., between 50 and 100°C) and moisture conditions, cure speed might be expected to increase significantly because of the formation of amine derivatives. Catalysts could be employed to further increase reaction speed.

As with PF or PRF systems, isocyanate polymers may not need to be highly crosslinked to achieve satisfactory bond quality. Studies with isocyanate cured plastics demonstrate that some isocyanate groups do not react fully until higher cure temperatures are reached (Darr et al., 1966). In polymeric MDI-wood combinations at five percent mc some evidence exists that cure may involve two stages et al., 1980). The first stage occurs at relatively moderate temperatures (up to 100°C) and provides acceptable bond strengths. The second stage involves higher temperature cure (100 to 200°C) where further crosslinking of the isocyanate system take place, possibly through the formation if isocyanates (cyclic isocyanates).

Standard waferboard bonding trials confirm laboratory findings that cure can occur at lower press temperatures, while under normal pressing conditions a 20 to 30 percent decrease in press time can be achieved over PF resins (Ball, 1981; Udvardy, 1979). The thicker the board, the greater the press time savings.

Experiments with a steam pressing technique have demonstrated the advantages of this system for bonding thick composite panels (Geimer, 1985). For instance, with PF adhesives a ½-inch thick board could be pressed in 90 seconds compared to the conventional 3½ minutes. Using isocyanates this press time can be reduced further to 40 seconds. Steam injection also has the added advantage of introducing moisture into the mat, which may accelerate the total isocyanate reaction.

Another possible cure technique is the application of radio frequency (RF) heating; however, little information is available on the use of this method to bond isocyanate wood composites. Sensitivity or RF to high mc levels (above 12 percent) may be a limitation here.

Dimensional Stability. Both low viscosity and surface tension properties of polymeric MDI cause it to readily penetrate into the wood surface during application. While this behavior causes problems when bonding solid wood, due to glue loss from the wood surface, with thin wafers the penetrating adhesive ends up on the other surface of the water, thus remaining available for bonding. This rapid penetration behavior,

together with the reactivity of polymeric MDI, likely results in fewer wood hydroxyl sites being available to interact with water. As a consequence, boards bonded with isocyanates tend to be more moisture resistant and dimensionally stable than those bonded with conventional adhesives (Deppe, 1977; Motoki et al., 1985). This mechanism is also reflected in the reported improvements in decay resistance of isocyanate boards over others (Deppe, 1977; Motoki et al., 1984).

Durability. The limited service history of commercial isocyanate boards makes it difficult to confidently assess the long-term durability of such panels. Experience with particleboard panels over the last 10 years supports the view that isocyanate boards are durable in exterior exposures (Deppe, 1977; Ernst, 1985). It should be remembered, however, that these panels are often three-layer boards with PF adhesive bonded faces and resin contents ranging from 6 to 11 percent. There also have been reports that boil test results, while satisfactory, show a greater loss in bonding properties compared with dry conditions than do fully PF bonded boards (Frisch et al., 1983). Long-term durability information on isocyanate-bonded waferboard and OSB is presently unavailable. Based on short-term accelerated aging tests, these boards generally performed as well or better than PF bonded panels (Motoki et al., 1984).

Both polyurethanes and polyureas have chemical linkage which can be susceptible to hydrolysis, especially at higher temperatures. The aromatic character of polymeric MDI will improve hydrolysis resistance but whether the resulting crosslinked structure is as durable as phenolic over long-term outdoor exposure remains to be fully established. Certainly, the relative proportion of polyurea to polyurethane formed during bonding will likely influence final board durability.

Creep is another durability related board parameter needing serious consideration, especially as interest in structural composite board products increases. Tests on high resin content V-100 type (German DIN requirement) particleboard indicates that creep properties are similar to PF boards (Deppe, 1977). Creep testing of PF bonded waferboard and OSB is presently underway which hopefully will be extended to include isocyanate boards as they become available in future. Degree of cure and resin content of the boards is expected to impact significantly on creep behavior. Current resin contents of less than 1.5 percent suggested for isocyanate boards may well be too low to attain desired creep properties.

3.5.3 Advantages and Limitations

A summary of potential advantages and limitations of utilizing isocyanates as binders for composite boards is presented in Table 7.

3.5.4 Future Directions

It is evident from this review of isocyanate adhesive application in wood composites that utilization of this binder system will increase in future, especially as chemical costs decline. Isocyanates usage will likely become prominent in situations where wood bonding problems need to be overcome; for instance, when high density or high extractive content wood species are used or when specialty overlays are bonded to

Table 7

Some Advantages and Limitations of Using Polymeric MDI Adhesives in Wood Composites

Advantages	Limitations
- good strength	- need to protect material from moisture during storage
- Variety of formulations	- cost
- both cold and hot temperature	- potential health and handling hazard
- fast press times	- tendency to cause board sticking to press and cauls
- tolerant to high mc furnish	- poor tack properties
- no formaldehyde emissions	- difficult to clean up
- reduce resin levels possible	

waferboard/OSB surfaces. Questions concerning exterior durability, creep properties and proper handling and storage techniques for isocyanates will certainly need to be resolved in the near future.

A variety of different possibilities exist for further isocyanate developments in wood bonding applications. Briefly, some of these options are:

Steam Injection Pressing. Cure advantages have already been demonstrated in the laboratory with this system. Since isocyanates cure rapidly and react with water, adhesive washout tendencies are less likely than with other resins. If commercialization is possible, steam injection will be highly favored for thick board pressing.

Catalyst Utilization. Catalyst incorporation into wood or resin offers further improvements in cure speed and the capability of directing the types of bond linkages formed. With steam injection, inclusion of ammonia or other gaseous amines in the vapor stream provides a potentially simple means to further accelerate cure.

Co-reaction with Formaldehyde. Formaldehyde is capable of reacting with the aromatic components of polymeric MDI to form methylol groups which are sites for further crosslinking. For example, addition of formaldehyde by inclusion of paraform or hexamethylenetetramine in the furnish may improve cure speed or durability of the adhesive. Excess formaldehyde addition, however, should be avoided to prevent board emission problems in service.

Co-reaction with other Polymers. Formation of prepolymers of isocyanate with other polymers such as polyglycols, PF or epoxys could provide co-polymer systems with unique application or bonding properties.

Utilization of Blocked Isocyanates. Blocked isocyanates are a special class of isocyanate precursors which are protected from reacting at ambient temeratures, but at higher temperatures "deblock" to regenerate the reactive isocyanate. In this manner isocyanates can be used in even higher mc environments or on wood material which has been moderately heated.

Whether any of these options are technically feasible remains to be proven. Certainly, the factors of competition, economics and processing requirements will influence the future of these and other options for utilizing isocyanates in wood composites.

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APPENDIX I

MATERIAL SAFETY DATA SHEET

MATERIAL SAFETY DATA SHEET

MOBAY CHEMICAL COMPANY
PITTSBURGH, PENNSYLVANIA 15205

SECTION I

MANUFACTURER'S NAME: MOBAY CHEMICAL CORPORATION	EMERGENCY TELEPHONE NO: (412) 923-1800
ADDRESS (Number, Street, City, State, and ZIP Code): Penn-Lincoln Parkway West, Pittsburgh, Pennsylvania 15205	
CHEMICAL NAME AND SYNONYMS: Mondur MR	TRADE NAME AND SYNONYMS: E-346
CHEMICAL FAMILY: Polymeric isocyanate	FORMULA:

SECTION II HAZARDOUS INGREDIENTS

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	TLV (Units)
Diphenylmethane diisocyanate	~50	0.02 ppm
Higher polymers of similar structure	~50	not established

SECTION III PHYSICAL DATA

BOILING POINT (°F) @ 5 mm Hg: 406 (208°C)		SPECIFIC GRAVITY (H_2O=1):	1.24
VAPOR PRESSURE (mm Hg): @ 25°C	$< 1X10^{-3}$	PERCENT VOLATILE BY VOLUME (%):	
VAPOR DENSITY (AIR=1):		EVAPORATION RATE (_____=1):	
SOLUBILITY IN WATER:	Insoluble		
APPEARANCE AND ODOR: Brown viscous liquid - odor, very slightly aromatic.			

SECTION IV FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used): 415°F (213°C) C.O.C.	FLAMMABLE LIMITS: Fire point-450°F (232°C) C.O.C.	Lel	Uel

EXTINGUISHING MEDIA
CO_2, dry chemical, chemical foam or water-fog may be used.

SPECIAL FIRE FIGHTING PROCEDURES
The usual fireman's body protection should be worn as well as self-contained breathing apparatus to protect from vapors formed from the product.

UNUSUAL FIRE AND EXPLOSION HAZARDS

SECTION V HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE
0.02 ppm for Diphenylmethane diisocyanate.

EFFECTS OF OVEREXPOSURE Mucous membrane irritation, tightness of chest, irritation of respiratory tract, coughing, headache, shortness of breath. Exposure can lead to allergenic sensitivity.

EMERGENCY AND FIRST AID PROCEDURES
Skin-wash with soap and water at least 5 minutes.
Eyes-wash with large amounts of water for minimum of 15 minutes - consult eye physician.
Internal-induce vomiting - consult physician.
Inhalation-remove to uncontaminated area - administer oxygen by authorized person if necessary.

SECTION VI REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID Avoid temperatures above 50°C (121°F) or below 0°C (32°F).
	STABLE		

INCOMPATABILITY (Materials to avoid) Avoid contact with water, alcohols, strong bases, metal compounds or surface active materials.

HAZARDOUS DECOMPOSITION PRODUCTS

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID Contact with moisture and other materials which react with isocyanates.
	WILL NOT OCCUR	X	

SECTION VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Absorb in an absorbant sweeping/cleaning compound (e.g. "oil dry") - remove from area in open drums and treat with water containing 1% ammonia before disposal.

WASTE DISPOSAL METHOD
Disposal of waste should be in accordance with federal, state, and local regulations regarding environmental control.

SECTION VIII SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type) Canister type gas masks equipped for organic vapors; masks supplied from external air source; self-contained breathing equipment.

VENTILATION	LOCAL EXHAUST	SPECIAL
To maintain vapor concentration below TLV.	MECHANICAL (General)	OTHER

PROTECTIVE GLOVES Chemically resistant rubber or plastic gloves.	EYE PROTECTION Chemical safety goggles.

OTHER PROTECTIVE EQUIPMENT
Safety showers and eye wash stations should be available.

SECTION IX SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING
This isocyanate should be protected from water by a dry atmosphere (-40°F Dew point) (-40°C) and maintained at 65°-75°F (180°-20°C).

OTHER PRECAUTIONS

11-8-74

EMERGENCY PHONE NUMBER
MOBAY CHEMICAL COMPANY 412-923-1800

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